February 26, 2004

Use Designations

For Chitosan-Enhanced Sand Filtration

Applicant Natural Site Solutions, LLC (NSS), Chitosan vendor and technical consultant

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Application Documents:

Application for Conditional Short Term Use Designation for Chitosan Enhanced Sand Filtration, July 1, 2003, Peter Moon, P.E. and Paul Geisert, P.E., Price Moon Enterprises, Inc. for Natural Site Solutions, LLC. (NSS)

Chitosan-Enhanced Sand Filtration. Engineering Report .with Addendum, NSS, May 15th, 2003

Chitosan-Enhanced Sand Filtration System. Operation and Maintenance Manual. NSS, April 30, 2003.

Toxicity Evaluations of Chitosan-based Products, Liqui-Floc and Gel-Floc: December 2002 and March 2003, AMEC Earth & Environmental Northwest Bioassay Laboratory, 5009 Pacific Hwy. East, Suite 2, Fife, WA 98424. (253) 922-4296.

Understanding the Freshwater Aquatic Toxicity of Chitosan When Used in Engineered Sand Filtration Stormwater Treatment Systems; March 27, 2003. John Macpherson, CPESC, NSS.

Analytical Testing Demonstrating the Inability of a Solution of Chitosan Acetate to Penetrate a Model Sand Filter; John Macpherson, NSS.

Quality Assurance Project Plan, Third Version, January 12, 2004, John MacPherson, NSS

Applicant's Use Level Request:

Interim Short-Term Use Designation for the operation of flow-through Chitosan-Enhanced Sand Filtration (CESF) technology for the reduction of turbidity in construction site stormwater.

Applicant's Performance Claims:

For construction site stormwater runoff with a turbidity of less than 600 NTU (influent), a properly engineered and deployed *Chitosan-Enhanced Sand Filtration System* will remove greater than 95% of the turbidity, producing effluent that will consistently meet the State surface water discharge standards.

Ecology Decisions:

Based on Ecology's review of NSS application submissions and the findings by the Technical Review Committee (TRC) Ecology is hereby issuing the following use designations for the CESF technology for adequately controlling small particulate turbidity (clays, silt, etc.) in stormwater discharges at construction sites:

1.General Use Level Designation for the CESF technology with the discharge of Chitosan acetate treated water to retention systems capable of infiltrating all storms to the ground with no discharge to surface water. The design of the infiltration system must be based on the criteria in Volume V of Ecology's 2001 Stormwater Manual for western WA. The design and operational criteria for the CESF specified in this document shall also be strictly adhered to. Records showing that total retention was achieved must be kept on site.

2.General Use Level Designation for the CESF technology with a discharge of Chitosan acetate treated water from a temporary holding pond to surface water only after the treated stormwater is demonstrated to contain less than 0.1 ppm residual Chitosan acetate polymer or is non-toxic to aquatic organisms (batch treatment). The design and operational criteria specified in this document, and in BMP C 250 of Ecology's Western WA Stormwater Manual shall be strictly adhered to. The effluent turbidity and pH shall be monitored at a frequency acceptable to Ecology.

3. Conditional Short-Term Use Designation (CUD) for the CESF technology with the chitosan acetate treated discharges conveyed directly or indirectly to surface water (flow-through system). This CUD expires on December 31, 2005, unless extended by Ecology and takes effect when all the applicable “Conditions" and

"Design and Operational Criteria" specified in this designation document are implemented or satisfied**.** This CUD will take effect on March 9, 2004 and will be posted at Ecology's stormwater web site as soon as possible.

4. Discharges from the CESF system under these designations:

- shall not cause or contribute to a violation of State Water Quality Standards,

- shall comply with the discharge requirements of the State of WA Construction Stormwater General Permit, AKART, and local government requirements, for turbidity and other applicable pollutants. This designation document must be used as the basis of SWPPPs for all construction projects where chitosan treatment is planned.

- shall be consistent with the guidance in BMP C250, Construction Stormwater Chemical Treatment, of Ecology's 2001 Stormwater Management Manual for western WA.

- are expected to achieve performance goals of a minimum of 95% reduction of NTU turbidity, a maximum discharge of 10 NTU turbidity, and a discharge pH within a range of 6.5-8.5. If these values are exceeded at any time the responsible site operating personnel shall immediately take appropriate corrective actions.

5. This CUD for discharge directly to surface waters applies to a CESF system using Liqui-Floc, a chitosan acetate based product, as specified in the findings and conditions sections of this CUD and <u>does not apply</u> to the use of Gel-Floc, a chitosan lactate, which is applied differently than the Liqui-Floc.

6. This CUD is a determination of the development level of this technology as determined by Ecology and its Technical Review Committee. For additional information and definitions refer to the CTAPE at Ecology's web site. Permit issuances and administrative orders by Ecology and local governments must be pursued separately by the project proponent (Developers, contractors, etc.)

7. Ecology hereby approves the NSS QAPP, Version 3, dated January 12, 2004 for completing the field and laboratory testing and submittal of a TEER needed to achieve a General Use Level Designation from Ecology for direct discharge to surface water from the CESF.

<u>Chemical Technical Review Committee (CTRC) Finding:</u>

The CTRC finds sufficient evidence to recommend to Ecology to grant Natural Site Solutions a CUD for a flow through CESF technology that can remove turbidity from stormwater at construction sites within acceptable

limits. The CTRC has also approved the NSS QAPP, Version 3, dated January 12, 2004.

Findings of Fact

1. A CESF system charged with #30 crushed silica sand has demonstrated the ability to reduce turbidity caused by the disturbance of sediment on construction sites by 97.44 percent (overall average) when operated at a flow rate of approximately 15 gallons per minute per square foot of filtration surface area. This translates to a flow rate of approximately 500 gpm when using a 48-inch diameter, 4-pod sand filter module Field results in table 1 also show NTU discharge levels from 1-12 with an average of 4.

2. Influent turbidity levels above 600 NTU demonstrated the potential to cause a slow degradation of the turbidity removal performance by the system resulting in eventual system failure. CESF systems shall be limited to influent turbidity levels of 600 NTU or less. Turbidity levels above 600 NTU shall be allowed additional settlement time or be pretreated in another manner not covered in this application for Conditional Use Designation.

3. Water with a pH range outside the CESF treatment window of 6.5 to 8.5 shall be pretreated to achieve this range. This pretreatment process is not covered in this application for Conditional Use Designation.

4. In the CESF treatment systems that have been constructed and operated to date no aquatic toxicity has been observed in the treated filtrate, (see table 2)

5. The Chitosan acetate polymer component, used for water treatment, is non-toxic to humans and other mammals, which makes it somewhat unique in the universe of treatment agents. Chitosan acetate does, however, exhibit toxicity to rainbow trout and should therefore be used at a maximum dose rate of 1 mg/L as Chitosan Acetate as a conservative measure to ensure no possibility of toxicity to rainbow trout in receiving water. (see table 3)

6. NSS provided a design/operation/maintenance manual, which includes information on selecting, sizing, assembling, operating and maintaining a CESF system.

7. NSS provided a list of CESF systems installed in Washington State.

8. NSS provided a significant amount of aquatic toxicity data demonstrating that the discharge residual of the Chitosan acetate polymer is expected to be within toxicity levels acceptable to Ecology when used as directed. (see table 5)

9. NSS provided other supporting information including system limitations and constraints, system specifications and warranty information.

Conditions applicable to flow-through CESF under this CUD

1. The approved Quality Assurance Project Plan (QAPP), dated January 12, 2004 must be followed and includes:

    - A procedure for analyzing residual chitosan-The analytical procedure for residual chitosan must be acceptable to Ecology or a qualified expert in the field of analytical chemistry,

    - Additional bioassay testing that is acceptable to Ecology's Randy Marshall including one in-situ bioassay test. Laboratory-based EC25 testing will also be necessary for the following receiving water conditions:

        - juvenile salmonid or other fish rearing or habitat,
        - salmonid or other fish spawning,
        - lakes,
        - marine waters,
        - sensitive marine habitat.

Note; The bioassay test protocols must be pre-approved by Ecology's Randy Marshall and typically will include EC25 and 7-day survival determinations, including testing with embryos. The tests could be conducted <u>once</u> either before a project SWPPP is prepared or ASAP to finish the bioassay testing for the projected receiving waters. If toxicity is revealed NSS will notify Ecology immediately that it set Chitosan use restrictions to the degree applicable for that particular species and receiving water.

- a selection process for pretreatments for influent turbidities above 600 NTU,

- a clear explanation (including appropriate graphics) of the relationship between pH and Chitosan effectiveness for turbidity removal. It is desirable to illustrate the decrease in effectiveness when the pH approaches the optimum of 6.5-8.5.

- the sand filter operating indicator(s) for switching to the backwash cycle (pressure drop, effluent turbidity, etc.) The chitosan dose rate shall not exceed 1 mg/L (as chitosan acetate by weight) or 100 mg/L as 1% Liqui-Floc and not exceed 50 mg/L as 2% Liqui-Floc.

2. Water quality influent and effluent shall be continuously monitored for pH and turbidity and the effluent for chitosan concentration and/or aquatic toxicity as follows: *(NOTE: All aquatic toxicity test procedures must be approved by Ecology's Randy Marshall prior to implementation).* For the continuous flow through discharge to surface water under the CUD the following monitoring and operating procedures shall be strictly followed at all sites until a General Use Level Designation is issued by Ecology:

a. The metering pump must be calibrated at startup of the CESF and every four hours during the operation of the Chitosan metering pump to ensure that the dosage is at or below 1.0 ppm at all times. All calibration results must be recorded simultaneously with the flow rates and the records kept on site.

b.The discharge from the sand filters must be maintained below 0.1 ppm residual chitosan acetate polymer at all times. At least two discrete grab samples of a homogeneous sand filter discharge must be collected during each operating period (CESF continuous operation up to 24 hours) and analyzed for residual Chitosan polymer. The samples must be collected one and two hours after the onset of each operating period.

c. In the event that the chitosan residual in the discharge is greater than 0.1 ppm, or the discharge exhibits aquatic toxicity based on approved bioassay testing, or when the CESF system is upset or fails a contingency plan to immediately correct the problem must be included in every SWPPP under this CUD. The contingency plan can include any of the following emergency operational measures, or equivalent measures for the handling of the "off-spec" stormwater:

- temporary storage sized to handle all reasonable failure scenarios,
- discharge to a sanitary sewer if available and pre-approved by the sewer authority,
- discharge to an infiltration system with no discharge to surface water, or,
- truck hauling for proper disposal until the problem is corrected.

d. At one or more construction sites and at any site that is not monitored for residual chitosan in the sand filter discharge operate an insitu bioassay test following a protocol that has been approved by Ecology (Randy Marshall).

e. At all construction sites, at the end of each 8-hour shift, a delegated responsible person must record his/her assessment of the operational efficiency of the CESF process and all upsets, the insitu bioassay results (where applicable), the sand filter discharge chitosan concentrations (where applicable) and any other relevant observations that relate to CESF proper

operation and must also certify the acceptability of the CESF discharge to surface water.

f. Stormwater discharges from the CESF system shall not cause or contribute to receiving surface water quality violations. If the discharge from the CESF will be to a fish spawning area in the stream an approval for that discharge must be obtained from the responsible Ecology Regional Office. NSS guarantees that CESF, when used as directed, will not produce treated water which exhibits aquatic toxicity caused by Chitosan added as a treatment agent.

3. Source Control procedures will be implemented to the maximum extent feasible to minimize the need for Chitosan treatment and for controlling the influent NTU to less than 600.

4. During periods of operation of the CESF system a qualified operator acceptable to NSS must be present on-site.

Design and Operational Criteria Applicable to Conditional Use and General Use Designations

1. The CUD and GULD apply only to Vanson/HaloSource Storm Klear Liqui-Floc (1% and 2% chitosan acetate) Chemical Abstract Service number 9012-76-4.

2. Because of the high solids loading in water associated with construction site runoff CESF systems must be designed and operated at a flow rate not to exceed 15 gpm per square foot of sand bed filtration area and should employ a minimum of three (3) sand filter pods to ensure adequate backwashing capacity. The backwash slurry from the sand filters must be discharged to a detention cell that is separate from the temporary storage cell for the incoming turbid stormwater. The overflow from the backwash slurry detention cell can overflow into the detention basin for the turbid stormwater.

3. The maximum suspended sediment (expressed as turbidity) of the influent water should not exceed 600 NTU.

4. The CESF system treated water output shall be equipped with an automatic integrated turbidity and pH sensors capable of shutting the system down if output turbidity or pH exceed preset values. An audible alarm and warning light will be installed on the treatment system to alert the operator in the event of a system failure. NSS is encouraged to include a computerized controller (like the Talus system) to automatically adjust chitosan dosage based on turbidity, flow, and pH.

5. The only filtration media approved is a pre-washed #30 crushed silica sand with a mean effective sand size of 0.34 mm and a filtration quality mesh of 230-400. Minimum sand bed depth shall be 18-inches underlain with a minimum of 6-inches of 1-inch crushed rock. An intermediate mesh-size garnet may be added to enhance performance.

6. Chitosan injection shall be performed with an LMI-brand C77, high viscosity pump head, electric metering pump, or equivalent. The CESF system shall include a flow-regulating valve on the input to and output of the sand filter. These regulating valves will reduce the maximum output of the pump as required and facilitate proper backwash.

7. The CESF system (including metering pump, chitosan storage and instrumentation) shall be completely enclosed in a secure structure with locking door. The Chitosan liquid concentrate tank, metering pump and tubing shall be completely contained for secondary containment. The metering pump discharge tubing shall have an anti-siphon valve.

8. Jar tests will be conducted, as needed, to confirm the dosage level of Liqui-Floc.

9. During the planning (SWPPP preparation, etc.) of a project the adverse potential impact on chitosan efficiency of the use of anionic polymers for soil blanketing and stability, will be evaluated.

10. The CESF system shall only be operated by a trained technician certified through an approved training program including classroom and field instruction. Training to be provided by Natural Site Solutions to include the following Minimum Training Requirements:

    Prerequisites:

    - Minimum 1-year experience with, and sound working knowledge of, high-pressure sand filter systems.
    - Experience deploying and troubleshooting pressurized water pumping and piping systems.
    - Fundamental knowledge of stormwater discharge regulations for applicable region/locale.
    - Fundamental knowledge of stormwater quality testing procedures and methods for parameters applicable to the region/locale.

Classroom – 4 hours

- Stormwater regulatory framework and requirements
- Stormwater treatment chemistry (chitosan, pH, coagulation, filtration, etc.)
- Stormwater treatability (how to do jar testing)
- Treatment system components and their operation
- Treatment system operation
- Troubleshooting

In the field – 40 hours

- Operating the treatment system

- Entering data in the system operations log
- Testing turbidity and pH
- Optimizing chitosan dose rate
- Water quality sampling and testing (turbidity and pH)

Summary of Turbidity Reduction Performance

Natural Site Solutions (NSS) has set up, operated and monitored the performance of 5 Chitosan-Enhanced Sand Filtration (CESF) systems between 2001 and 2003 in the state of WA. Based on the raw data sheets, the 235 sample pairs collected during the study represent the treatment of approximately 599,500 gallons of water. Over the duration of the 5 projects a total of approximately 286,300,000 gallons of water were treated and discharged.

Table 1. CESF TURBIDITY REDUCTION PERFORMANCE STATISTICS

Treatment Site	# of Paired Samples	Influent Average (NTU)	Effluent Average (NTU)	Average Treatment Efficiency (%)	95% Confidence Range (%)	
Lowe's	19	49	6	87.98	87.57	88.40
WSDOT	19	43	2	95.17	93.30	97.04
Crosswater	38	458	12	97.27	96.63	97.90
Lakeside Sand and Gravel	38	55	1	98.68	98.54	98.83
Lakeside Development	121	208	2	98.95	98.87	99.03
Overall	235	198	4	97.44	97.01	97.87

The data in table 1 indicate an overall turbidity reduction efficiency of 97.44 percent with a 95 percent confidence range between 97.01 and 97.87 percent.

Aquatic Toxicity of Field Samples

A total of 30 acute whole effluent aquatic toxicity tests were performed on treated water samples collected during field tests. Species tested included Rainbow Trout, Fathead Minnow and Daphnia Magna. Five of the 30 tests resulted in less than 100 percent survival of the tests organisms. These ranged from 92.5 to 97.5 percent survival but were not statistically significant when compared to the control organisms. The bioassay tests were performed using Ecology approved test methods and the quality assurance/quality control parameters appear to have been met in each test. (see table 2)

Table 2. CESF WHOLE EFFLUENT AQUATIC TOXICITY TEST RESULTS

Project	Acute Rainbow Trout	Acute Fathead	Acute Daphnia Magna

	Toxicity[1] % Survival	Minnow Toxicity[1] % Survival	Toxicity[1] % Survival
Lowe's Hardware Construction	100	95	100
WSDOT Sunset Project	100	100	100
Crosswater Housing Development	100	100	100
	100	97.5	100
Lakeside Sand & Gravel	100	95	92.5
	100	100	100
Lakeside Development	97.5	NT	100
	100	NT	100
	100	NT	100
	100	NT	100
	100	NT	100
	100	NT	100

1. Test Methods: Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 4th Edition (EPA/600/4-90/027F).

   Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria, revised December 1998 (Washington State Department of Ecology Publication No. WQ-R-95-80).

Whole Product Aquatic Toxicity Testing Evaluation:

The AMEC December 2002 study was performed using moderately hard synthetic water (MHSW) for the Fathead minnow and Daphnia pulex tests and filtered City of Fife tap water for the Rainbow trout. (Table 3)

TABLE 3. AMEC DECEMBER 2002

CHITOSAN ACETATE	ACUTE RESULTS		
Evaluation	Fathead Minnow MHSW[2]	*Daphnia pulex* MHSW[2]	Rainbow Trout filtered tap water
Control % Survival	100	95	100
NOEC (mg/L)	5.0	10.0	0.10
LC50 (mg/L)	6.43	13.69	1.10
Reference Toxicant	Acceptable	Acceptable	Acceptable

1. Results calculated using the Probit method.
2. Moderately Hard Synthetic Water

Method: EPA. 1993. EPA/600/4-90/027F, August 1993

This was the only study that was not disqualified by Ecology and was performed using the EPA test method approved in Ecology's 2002 TAPE outlined on page 37 (Table C-1).

Turbid Water Testing

Another study (AMEC March 2003) used only Rainbow trout (the most sensitive species) and included a chronic test in clean MHSW and another chronic test where high doses of chitosan were added to turbid water then tested (at the request of Randy Marshall). In the turbid water test the chitosan was added to water containing bentonite clay, allowed to settle then filtered through a standard coffee filter. This filtered decanted water was then used for toxicity testing. They represent only an approximation of how much of an overdose of chitosan it would take in order for the treated decanted filtrate to exhibit toxicity to trout. We believe this information has significant value as long as it is clearly differentiated from the true chitosan LC50 and NOEC of 1.1 mg/L and 0.10 mg/L, respectively.

TABLE 4. AMEC MARCH 2002

CHITOSAN ACETATE	**ACUTE RESULTS**		
Evaluation	*O. mykiss* (Rainbow Trout) MHSW[1]	*O. mykiss* (Rainbow Trout) in simulated turbid stormwater[2]	
Control % Survival	100 %	100 %	
	NOEC (mg/L) 1.0	100	
	LC50 (mg/L)4.34	>100	
Reference Toxicant	Acceptable	Acceptable	

1. Moderately Hard Synthetic Water
2. Prepared by mixing 1-gram bentonite clay per liter of MHSW. (These Chitosan Acetate concentrations represent the initial dosages in the turbid water and not toxicity levels)

Method: EPA Draft Method. 1994. EPA/600/4-91/002

It is important to note that the above results were generated using a draft EPA test method (there are currently no approved chronic trout toxicity test methods).

PME, Inc. believes that all LC50 and NOEC aquatic toxicity testing of chitosan acetate be performed using MHSW. Unfortunately, the only trout test performed with MHSW was performed using a test method that is not approved under Ecology's 2002 TAPE. For this reason PME recommends that the interim rainbow trout acute LC50 and NOEC values be taken from the AMEC December 2002 (revised January 2003) study. Those values are LC50=110 mg/L as 1% Liqui-floc and NOEC=10 mg/L as 1% Liqui-floc. During the Conditional Use period PME recommends performing the LC50 and NOEC tests using MHSW (EPA.1993. EPA/600/4-90/027F, August 1993) in an effort to standardize the method so that it may be reliably reproduced. PME also recommends that the same test be performed using actual receiving water from a specific project to gain an understanding of chitosan toxicity in a specific water body. Finally, the results reported from the simulated turbid water study should be viewed as a failure analysis, not a product LC50. It was designed to determine the

concentration of chitosan at which the resultant treated filtrate would exhibit toxicity to rainbow trout.

Mitigation of Chitosan Toxicity

There has been a concern that the chitosan added to the water before the sand filter may migrate through the sand filter and be discharged with the filtrate. NSS has performed a bench-scale treatment test to show that this is not true. Chitosan acetate clearly coagulates finely divided suspended sediment, is adsorbed to the surface of these coagulated particles, then is captured in the bed of the sand filter. Periodically, the chitosan/sediment particles are removed from the sand filter in the backwash cycle.

The results of the lab test show that 2.0 mg/L Chitosan becomes bound to the sand in the sand filter and does not exit with the clean filtrate. The test was run with clean water rather than turbid water to create a worst-case scenario. In dirty water the chitosan rapidly binds to the suspended sediment and is retained in the sand filter. This test was designed to show that, even in clean water the Chitosan will bind to the sand in the absence of suspended sediment.

Table 5.

TEST	VOLUME FILTERED	FILTER WEIGHT BEFORE (GMS)	FILTER WEIGHT AFTER (GMS)	WEIGHT OF CHITOSAN (GMS)
Blank # 1	5 liter	0.318	0.319	0.001
Blank # 2	5 liter	0.312	0.312	0.000
Blank # 3	5 liter	0.315	0.316	0.001
Std. # 1 (10 mgs chitosan)	1 liter	0.315	0.324	0.009 (90% recovery)
Std. # 2 (10 mgs chitosan)	1 liter	0.315	0.324	0.009 (90% recovery)
Std. # 3 (10 mgs chitosan)	1 liter	0.313	0.321	0.008 (80% recovery)
Sand Filter	5 liters	0.319	0.320	0.001
Sand Filter	5 liters	0.317	0.317	0.000

The blank samples were run with the same water source used in the sand filter tests to determine the background weight present in the water. The pH of the blanks was raised to 11.0 prior to filtration exactly as the sand filtered water was (with 10% sodium hydroxide solution). The blank results indicate a possible background weight of 0.001 gms.

The standards were run with the same water source used in the sand filter tests but spiked with 10 mgs of chitosan. An average of 87 % of the chitosan was recovered in these tests demonstrating the ability to recover chitosan at pH 11.0.

The sand filtered water started out with 10 mgs chitosan per 5 liters (2 mg/L X 5 L = 10 mgs). After sand filtration the first 5 liters analyzed showed 1 mg (not statistically significant compared to the blanks) and the second 5 liters showed no weight gain at all. These results indicate that no measurable quantity of chitosan penetrated the sand filter bed to be discharged in the filtrate.

Description of the Technology:

Chitosan-enhanced sand filtration (CESF) is a stand-alone construction site water treatment technology, which is comprised of four basic components:

- Stormwater transfer pump
- Chitosan addition
- Pressurized multi-pod sand filtration
- Interconnecting treatment system piping

CESF is a flow-through stormwater treatment technology (attached Figure) that utilizes chitosan, a natural biopolymer, in conjunction with pressurized sand filtration to remove turbidity (suspended sediment). Each treatment system is designed and installed to operated on an as need basis, pumping water from a retention basin whenever the water level of the retention basin is high enough to warrant processing. When stormwater is transferred from the retention basin to the sand filtration unit, chitosan is introduced to stormwater to coagulate suspended solids producing larger particles, which are retained within a sand filter. The filtration systems are equipped with automatic backwash systems, which will backwash the collected sediment from the individual filter pods as necessary to maintain the hydraulic capacity of the filtration media. This feature allows the treatment system to operate on a continuous flow-through basis.

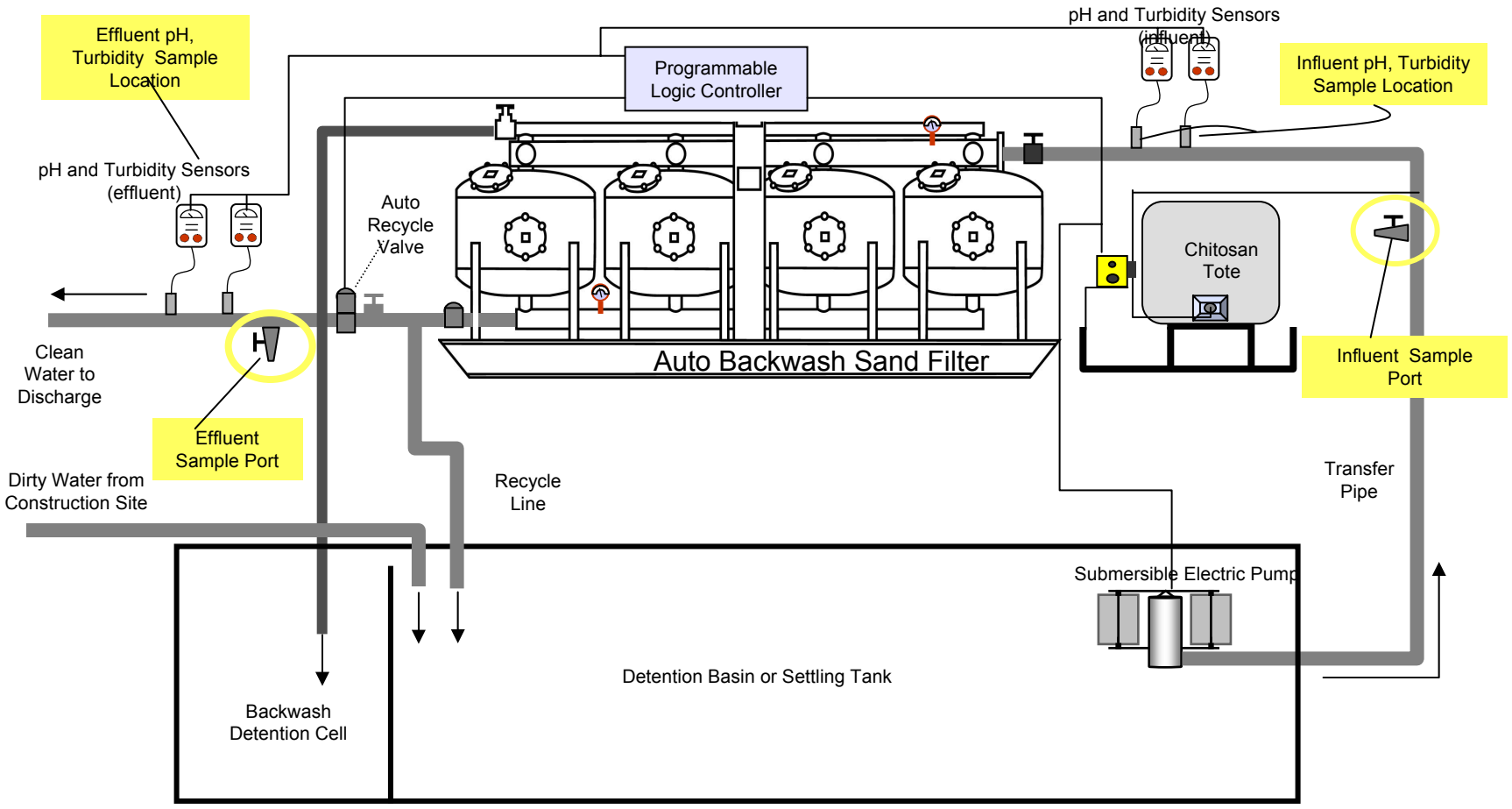

Figure 1
Chitosan-Enhanced Sand Filtration System Schematic

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O&M Manual: http://www.naturalsitesolutions.com/PDF/Chitosan_O_M_Manual.pdf

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